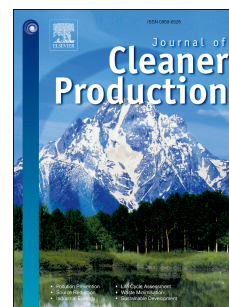


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Application of highly carboxylate resins in aqueous emulsion for leather coating avoiding the use of isopropyl alcohol

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Abstract

Today, the first stages of the finishing processes of buffed cattle hides or full loose grain—known as impregnation—are largely carried out with acrylic resins and penetrating agents (typically, a mixture of surfactants and solvents). This application aims to strengthen the partially buffed grain layer bound to the rest of the dermis. To that end, a composition of emulsified acrylic resins is used, as well as a penetrating agent – usually isopropyl alcohol –, and water.

The process examined consists in the application of acrylic polymers in an aqueous emulsion that, because of their structure, size, and properties no longer require the use of the isopropyl alcohol contained in the penetrating agents. The use of this alcohol causes adverse effects on the health of workers that are exposed to emanations of isopropanol vapors (irritant to eyes, respiratory tract, and skin) in the work environment. Effects from prolonged exposition and inhalation may lead to headaches, dizziness, drowsiness, nausea and, ultimately, to unconsciousness.

By using the new polymers developed in this work, the negative environmental effects of the finishing process can be minimized. At the same time, the use of these highly carboxylate resins avoid the exposure to isopropyl alcohol, which is harmful to the health. In addition, the volatile organic compounds (VOC) are reduced without compromising the appearance, performance and fashion requirements that are expected in the final product.

Keywords: Carboxylate resin; impregnation; isopropyl alcohol; leather finishing

1. Introduction

The demands of the market increasingly require the tanning industry to use less harmful products for the human health as well as more environmentally-friendly practices (Kolomaznik et al., 2008; Herva et al., 2011). In addition, the legislation requires the industry to follow guidelines to reduce the consumption of materials classified as hazardous or toxic (Directive 2000/53/EC; Dixit, 2015).

One of the main environmental and toxic hazards posed by the finishing process is the release of organic solvents into the atmosphere and contamination of water (Kurian et al., 2009). That is why it is important to eliminate or reduce the amount of solvent content in finished products today. The use of aqueous finishes instead of solvent-based finishes emerges as a solution to this problem (Bacardit et al., 2009; Ollé et al., 2014).

The process examined in this study is the impregnation. The impregnation is one of the first coats applied on the leather surface to improve the break of the full-grain leather or the buffed leather. This coat consists in applying high amounts of acrylic polymer dispersions to the surface of the leather (between 215 and 430 g/m²).

The impregnation technique involves the application of thermoplastic polymer dispersions that penetrate the leather and form a bond between the grain layer and the reticular layer, or between the buffed grain layer and the reticular layer.

Three conditions have to be met in impregnations: (a) the dispersion must humidify the leather; (b) it must penetrate rapidly and avoid the coalescence before obtaining sufficient penetration; (c) it must penetrate with the sufficient intensity so as to enable the welding between the reticular layer and the grain layer (i.e., 1/3 of leather thickness). With these conditions in mind, the addition of surfactants or penetrating agents is commonly required, which cause emissions of toxic vapors owing to their composition of volatile organic compounds. It is therefore critical to develop new solvent-free or low-solvent-content products by modifying finishing formulations and thus achieving the high

performance required for each of the items to be manufactured (Demir-Cakan et al., 2009).

Carboxylated acrylic resins are acrylate- and methacrylate based resins having free carboxyl groups in their composition. Carboxylated resins usually show optimum chemical resistance and adherence, in addition to excellent flexibility. These characteristics are needed to perform a good finish for leather.

In a previous work (Ollé et al., 2012), a series of carboxylated acrylate copolymer resins were prepared with different carboxylic groups distribution. The properties of the resulting acrylics vary depending on the nature of the alkyl groups of the monomers used in the polymerization.

The synthesis was carried out by free-radical polymerization. This polymerization involves long chain free radicals as propagating species, usually initiated by the attack of free radicals derived by thermal or photo-chemical decomposition of initiators. Polymerization proceeds by the chain reaction addition of free radical chain ends to double bonds of monomer molecules. Finally two propagating species (growing free radicals) combine or disproportionate to terminate the chain growth. Because of its versatility, synthetic ease, compatibility with a wide variety of functional groups, and its tolerance to water and protic media, free radical polymerization has been widely used in industry for the synthesis of various polymeric materials.

In the previous study mentioned above, four resins were synthesized varying the concentration of ethyl acrylate, butyl acrylate, and methyl acrylate acid. Sodium lauryl sulphate was used as emulsifying system. An experimental design was performed in order to choose the most appropriate combination of monomers. This combination can be seen in Table 1.

The amount of surfactant (i.e. sodium lauryl sulphate) was kept constant at 2 wt% in all the four syntheses carried out. Different properties were analyzed: hardness, penetration time and loss in leather softness. In all the three

properties studied, the most influential monomer is methyl acrylate acid. This monomer allows for obtaining less hard resins with faster penetration.

The best combination of monomers in order to obtain a well-balanced resin is 65% of ethyl acrylate, 30% of butyl acrylate and 5% of methyl acrylate acid. Using 5% of methyl acrylate acid, a highly carboxylated resin can be obtained. In addition, this new highly carboxylate resin enables leather impregnation without using surfactants or penetrating agents.

Following this line of research, the objectives of this paper are to study the synthesis and the application of new leather finishing acrylic resins for impregnation avoiding the use of surfactants and/or penetrating agents and to replace an industrial-scale formulation by a new formulation that complies with the European directive reducing pollution in wastewater, the atmospheric emissions and the toxicity to humans (Hu et al., 2008).

2. Materials and methods

2.1. Chemicals

The aims of this paper is to study the new synthesized highly carboxylate resin in aqueous emulsion versus a commercial impregnation acrylic resin to obtain a more sustainable and harmless finishing process without using isopropyl alcohol.

As explained in the introduction, the synthesis was carried out by free-radical polymerization. This is the most widely practiced method of chain polymerization and is used almost exclusively for the preparation of polymers from olefinic monomers of the general structure $\text{CH}_2 = \text{CR}_1\text{R}_2$, where R_1 and R_2 are two substituent groups which may be identical, although they are often different. The procedure by which an emulsion polymerization is carried out has a significant effect upon the resulting polymer and its properties. Indeed, polymers with quite different performance characteristics can be produced from the same reaction formulation by appropriately controlling the type of

polymerization process and the conditions. More specifically, in this work, the batch emulsion polymerization since polymers with higher molecular weight are obtained (Musyanovych et al., 2007; Bakhshi et al., 2009). In addition, batch emulsion polymerization has some clear advantages as compared to other types of free radical polymerization, being bulk, solution and suspension polymerization. These advantages are a relatively high reaction rate, a moderate viscosity increase for high solids polymerization and a relatively good control of heat transfer.

In the batch emulsion polymerization, all ingredients are added in the reactor at the beginning of the polymerization and an oil-in-water emulsion is formed. Figure 1 shows the reaction system. Polymerization starts at 20 °C and the temperature increases once the reaction has started. The temperature rises to a maximum depending on the type of monomers used in the polymerization.

The monomers used in the polymerization were ethyl acrylate (EA), butyl acrylate (BA), and methyl acrylate acid (MAA), and were supplied by Dow Chemical. Sodium lauryl sulphate was used as surfactant, and it was supplied by Kao Corporation.

Emulsions were prepared according to the following procedure: all the products (67.5 % water, 2% surfactant, and 25% monomers in the proportion of 65% of ethyl acrylate (EA), 25% of butyl acrylate (BA), and 5% of methyl acrylate acid (MAA)) were added to the reactor flask (1 liter capacity). Then, nitrogen was applied to the reactor, ensuring that all oxygen was dissipated. Afterwards, 0.0006%v of ferrous sulphate heptahydrate was added to the reactor to promote the reaction in a redox system (i.e., 0.1% ammonium persulphate and 0.07% sodium metabisulphite). The reaction was maintained at 85 °C for 30 min. Ferrous sulphate heptahydrate and ammonium persulphate were supplied by Dow Chemicals. Sodium metabisulphite was supplied by BASF.

The commercial impregnation acrylic resin contains 40% of solids and presents a glass transition temperature (T_g) of -31°C. It was supplied by BASF.

2.2. Experimental set-up

The test was carried out on Russian chrome tanned cattle hides shaved at 1.3-1.4 mm. The hides were first retanned using synthetic retanning agents and vegetal tannin. Then, the hides were fatliquored using ester phosphate, sulfonated beef tallow, and crude beef tallow. Finally, the hides were dried (vacuum-air) and buffed twice (consecutively) using buffing paper of 280 and 320 grit size.

Once the new resins were synthesized, they were applied to buffed bovine chrome-tanned leather explained above using a rollcoater. After buffing the hides, the dust is removed and leathers are impregnated using a solution of resin (i.e., 25% of resin in water). Leathers are left to stand for 24 hours to facilitate the even distribution of the solution.

The commercial impregnation acrylic resin is applied following the same processes as for the new synthesized polymers, but adding 10% of penetrating agent (i.e. isopropyl alcohol).

On a second stage of the study, both types of impregnation formulations were finished to obtain footwear leather. The finishing formulation is shown in Table 2.

2.3. Analytical methods

To determine the applied properties of the resins obtained, penetration time of the resin solution droplet was measured. To this end, a given amount of impregnation solution (i.e. 1 mL) is pipetted into each of the hide parts in which the structure of the collagen fibers are different in density: shoulder, belly, and butt. The time of penetration is taken in seconds and the measurements are made in triplicate.

After the industrial application of both resins (the new synthesized polymer and the commercial impregnation acrylic resin), VOC measurements were made to

determine the amount of IPA vapors (isopropyl alcohol) in the workplace environment (Cuadros et al., 2013). To that end, the following personal sampling equipment was used:

- Type-G personal air sampling pump according to UNE-EN 1232 standard. Gilair SN 105184 (M).
- Air flow meter. Bios Drycal DC-life M-Rev 1.08.
- Activated carbon filter tube (50/100) (batch 2000 SKC SN 4321618634 and SN 4321618639); 7 cm in length; outer diameter: 6 mm; inner diameter: 4 mm. The tube comprises 2 activated carbon sections separated by a 2 mm piece of polyurethane foam. The first section contains 100 mg activated carbon 20/40 mesh, and the second section contains 50 mg. A silanized plug of glass wool is placed before the first section, and a 3 mm piece of polyurethane foam is placed on the output end of the tube.
- An airflow of 0.2 L/h of air is pumped using the air sampling pump. The air passes through the activated carbon tube, and the vapors are trapped in the activated carbon filter.

The recommended exposure limit is, on average, 400 ppm for a 10-hour work period (400 ppm; 983 mg/m³ ACGIH 1990-1991) and 500 ppm, which cannot be exceeded in 15-minute work periods (500 ppm, 1230 mg/m³ ACGIH 1990-1991).

The amount of isopropyl alcohol trapped in the activated carbon filter was determined by gas chromatography following the analysis method based on the MTA/MA 016 A89-1 standard).

Once all finishing operations were carried out, the most important physical aspects were evaluated in accordance with the GERIC quality requirements for leather (Grouping of European Leather Technology Centers). The most important parameters assessed to define the quality of leather that was impregnated during the manufacturing process were the following:

-IUP 15. Measurement of water vapour permeability. Corresponding with ISO 14268:2002. In this test, a circular testing piece is placed into a small vessel containing a desiccant like silica gel. The testing piece is conditioned at 23 °C and 60% relative humidity overnight. The next morning the silica gel is removed and replaced by fresh silica gel. After weighing the vessel, the absorbency of water vapour from the standardised surrounding air is measured by weighing it after 8 h. The weight gain is divided by 8 and divided by the area of the testing vessel which has a constant size. The resulting value is a water vapour permeability measured as absorption of water vapour at the silica gel in mg/h.cm^2 .

-IUP 20. Measurement of flex resistance by flexometer method (dry and wet). Corresponding with ISO 5402:2002. This method determines whether the finish is vulnerable to cracking and other damage when the leather is flexed during use. A special double fold is applied to a sample of leather measuring 45 x 70 mm to give an "L" shaped test piece. The two ends are then clamped into the Bally flexometer. The machine subjects the leather to a relatively slow but very harsh creasing motion, which is focused along the centerline by the moving fold. After a predetermined number of flexes, the finish is evaluated for signs of cracking, delamination from the leather, and discoloration.

-IUF 412. Leather fastness test: change of colour with accelerated ageing. Corresponding with ISO 17228:2005. Over time, the surface colour of leather and the leather itself change due to ageing and to the action of the surroundings on the leather. The purpose of the various ageing procedures described in ISO 17228:2005 is to obtain an indication of the changes that could occur when leather is exposed to a certain environment for a prolonged time. The test conditions to be used depend on the type of leather and its intended use.

-IUF 450. Colour fastness of leather to dry and wet rubbing (50 rubs). Corresponding with ISO 11640. This method determines whether leather can stand up to being rubbed by clothing during use. The machine clamps strips of leather onto its horizontal metal platform under tension, and then subjects them to linear rubbing with a piece of standard wool felt pad. The test is performed with the felt rubbing pad under three conditions to mimic all possible conditions of normal use: dry, wet and wetted with artificial perspiration solution. After

testing, the degree of color transfer to the felt pad is assessed, and the amount of damage to the leather specimen is graded.

-IUF 470. Leather Test for adhesion of finish (dry and wet). Corresponding with ISO 11644:2009. Finish adhesion strength is the force required to peel away the finish from the underlying leather. It is determined by bonding the finished side of leather test strips to polyethylene ("plastic") plates using a solvent-free, heat-activated PU-based adhesive.

3. Results and discussion

3.1. Characterization of the new synthesized highly carboxylate resin

The synthesized resin has bluish white final color, which is an indication of small particle size. The composition of solids is around 25%, pH is 3, viscosity is of 11 seconds, and the density of 1.02 g/cm^3 . The characterization of the new resin can be seen in Table 3. Figure 2 shows the infrared spectrum of this resin.

3.2. Impregnation application

The function of impregnation is to promote the adhesion of grain and dermis and/or that of the buffed grain and dermis once they penetrate into the grain. The idea is to prevent grain loosening by filling the interfibrillary spaces of the leather structure and binding the tanned fibers of collagen together.

After applying the formulations mentioned in the experimental part, the penetration time of the dispersion into the leather was analyzed. The results are shown in Table 4.

An analysis of the results shows the difference in penetration time between highly carboxylate resins and commercial resins for impregnation. As can be observed, the ideal penetration time for impregnation applications is 8 to 10 seconds.

Due to the mismatch in the penetration time of the commercial resin, a scaling of the amount of penetrating agent was required to adjust the penetration times

to their industrial application. Three tests using 15, 20, and 25 parts of penetrating agent was made per every 100 g of commercial acrylic resin for impregnation. The results obtained are shown in Table 5.

After examining the results obtained, it is clear that to obtain similar results of penetration as those obtained using the new synthesized resin, the use of isopropyl alcohol is needed. The optimal formulation is 100 g of acrylic resin for impregnation and 25 g of penetrating agent.

In contrast, using the new synthesized resin 81 g of carboxylate resin and 19 g of water has to be applied. Then, the use of isopropyl alcohol is avoided.

3.3. VOCs analysis

As explained in the experimental part, in developing the industrial application, VOC measurements were made to determine the amount of IPA vapors (isopropanol alcohol) in the workplace environment.

The recommended exposure limit is, on average, 400 ppm for a 10-hour work period (400 ppm; 983 mg/m³ ACGIH 1990-1991) and 500 ppm, which cannot be exceeded in 15-min work periods (500 ppm, 1230 mg/m³ ACGIH 1990-1991).

The amount of isopropyl alcohol trapped in the activated carbon filter was determined (the analysis method is based on the MTA/MA 016 A89-1 standard by analyzing them through the HS-SPME-GC-MS method.

The chromatograms obtained are shown in Figure 3 and Figure 4.

As can be seen in the Figure 3 and 4, both chromatograms present three peaks at: 2.072-2.073, 2.554-2.551 and 3.396-3.339 min which correspond to the extraction diluent. The chromatogram of the measurement using the commercial acrylic resin shows a peak in 1.685 min which corresponds to isopropyl alcohol.

The values obtained from the measurement of vapors in the workplace environment can be seen in Table 6. As can be seen in Table 6, there is a

significant difference between both formulations, the new one using highly carboxylate resin and those using the commercial resin. Using the new synthesized resin, no isopropyl alcohol vapors are obtained. Instead, using the commercial resin, 22600 ppm of isopropyl alcohol vapors are obtained. This value exceeds in 4520% the recommended exposure limit (i.e. 500 ppm).

3.4. Physical properties

Once the optimal working conditions are established, the aim of this second stage of this study is to assess whether the leathers processed with this new system present advantages over the leathers finished using a commercial acrylic resin. In addition, we will check that the leathers meet the demands required for footwear. The results obtained are shown in Table 7.

As can be seen in Table 7, leathers finished with the new synthesized resin present similar results to those obtained with a commercial acrylic resin. The leathers meet the quality requirements for footwear, and are commercially accepted. Additionally, the new process avoids the use of isopropyl alcohol, and then, no vapors are emitted to the workplace.

From an economic perspective, a comparison of costs between chemicals, residual water disposal as well as machine cleaning costs to manufacture 100 m² of leather between the new formulation and the formulation using the commercial resin indicates that there are important differences between the two methods. These differences are detailed in Table 8.

Hence, the suggested coating formulation results in savings of up to 27%.

4. Conclusions

The industrial application of highly carboxylate acrylic resins for impregnations to footwear leather finishes proved to be effective. The replacement of conventional acrylic resins for impregnation by highly carboxyl acrylic resins resulted in a total elimination of organic vapors in the workplace. The 100%

reduction indicates a significant improvement in occupational health and environmental protection.

The results obtained from the assessments fully meet the quality parameters specified in the GERIC table of values. Indeed, none of the parameters is below the values of the GERIC table or below the values obtained by standard manufacture.

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| Resin | Ethyl acrylate | Buthyl acrylate | Methyl acrylate acid |
|-------|----------------|-----------------|----------------------|
| 1 | 0.7 | 0.25 | 0.05 |
| 2 | 0.55 | 0.4 | 0.05 |
| 3 | 0.5 | 0.4 | 0.1 |
| 4 | 0.7 | 0.2 | 0.1 |

Table 1. Experimental design

| | PARTS | PRODUCT |
|-----------|---|--|
| BASE COAT | 100 | Casein free aqueous pigment |
| | 50 | Casein based protein binder |
| | 200 | Water |
| | 75 | Wax emulsion |
| | 60 | Micronized dispersion of a silica complex for use in aqueous medium. |
| | 200 | Emulsified acrylic polymer |
| | 100 | Urethane polymer 1 |
| | 100 | Urethane polymer 2 |
| | 5 | Cross-linker |
| | Application 2 x Roller (107 wet g/m ²) | |
| TOP COAT | 75 | Urethane polymer 3 |
| | 25 | Urethane polymer 4 |
| | 50 | Urethane polymer 5 |
| | 100 | WATER |
| | 4 | Crosslinker |
| | Application 2 x spraying machine (43 wet g/m ²) Ironing at 80 °C - 80 kg/ cm ² - 1 second | |

Table 2. Formulation for buffed grain leather for footwear on impregnated leather

| EA 65% BA 25% MAA 5% | |
|--|---------------------------|
| Emulsion | |
| Color | Bluish white |
| Solids (%) | 24.64 |
| pH | 2.97 |
| Viscosity (seconds) | 11.0 |
| Free monomer | 36 ppm BA |
| Glass transition temperature (°C) | -27 |
| Density (g/cm³) | 1.0228 |
| Odor | Acrylic resin, pungent |
| Film | |
| Color | Translucent white |
| Aspect | Uniform, with white veils |
| Water absorption (%) | 106.2 |
| Hardness (°Shore) | 50.0 |

Table 3. Characterization of the new synthesized resin

| | | Shoulder | Belly | Butt |
|-------------------|---|----------|-------|------|
| Carboxylate resin | | | | |
| Puncture | A | 8 s | 7 s | 9 s |
| Puncture | B | 8 s | 7 s | 9 s |
| Puncture | C | 8 s | 7 s | 9 s |
| Average | | 8 s | 7 s | 9 s |
| Commercial resin | | | | |
| Puncture | A | 17 s | 16 s | 21 s |
| Puncture | B | 18 s | 16 s | 21 s |
| Puncture | C | 18 s | 16 s | 21 s |
| Average | | 18 s | 16 s | 21 s |

Table 4. Penetration time of the resins under study

| | Shoulder | Belly | Butt |
|--|----------|-------|------|
| 100 g resin + 15 g IPA (average 3 punctures) | 14 s | 14 s | 17 s |
| 100 g resin + 20 g IPA (average 3 punctures) | 12 s | 12 s | 14 s |
| 100 g resin + 25 g IPA (average 3 punctures) | 9 s | 9 s | 11 s |

Table 5. Penetration time of the commercial acrylic resin using isopropyl alcohol

| | Isopropyl alcohol vapors |
|--------------------------|--------------------------|
| Highly carboxylate resin | 00.0 ppm |
| Commercial resin | 22.6 ppm |

Table 6. Measurement of vapor concentration in the air of the workplace

| Test | Carboxylate resin | Commercial acrylic resin | GERIC Recommendations |
|---|--------------------------|---------------------------------|------------------------------|
| Permeability IUP 15 (mg/cm ² h) | 1.3 | 1.3 | Minimum 1.0 |
| Dry flex resistance IUP 20 (bends) | 100,000 | 100,000 | Minimum 50,000 |
| Wet flex resistance IUP 20 (bends) | 50,000 | 50,000 | Minimum 20,000 |
| Ageing resistance IUF 412 | 5 | 5 | Minimum 4 |
| Dry rubbing fastness IUF 450 | 5 | 5 | Minimum 4 |
| Wet rubbing fastness IUF 450 | 5 | 5 | Minimum 4 |
| Dry adhesion resistance IUF 470 (N/cm) | 8.0 | 7.8 | Minimum 4.0 |
| Wet adhesion resistance IUF 470 (N/cm) | 4.5 | 4.2 | Minimum 2.0 |

Table 7. Physical test results

| To manufacture 100 m ² of finished leather | New resin | Commercial resin |
|---|-----------|------------------|
| Chemicals | 144.73 | 174.25 |
| Wastewater treatment | 1.11 | 6.54 |
| Machine cleaning costs | 0.09 | 20.86 |
| TOTAL | 145.93 € | 201.65 € |

Table 8. Formulation costs

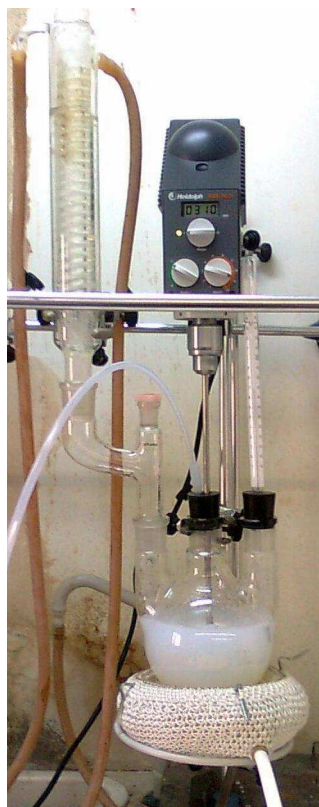


Figure 1. Reaction system

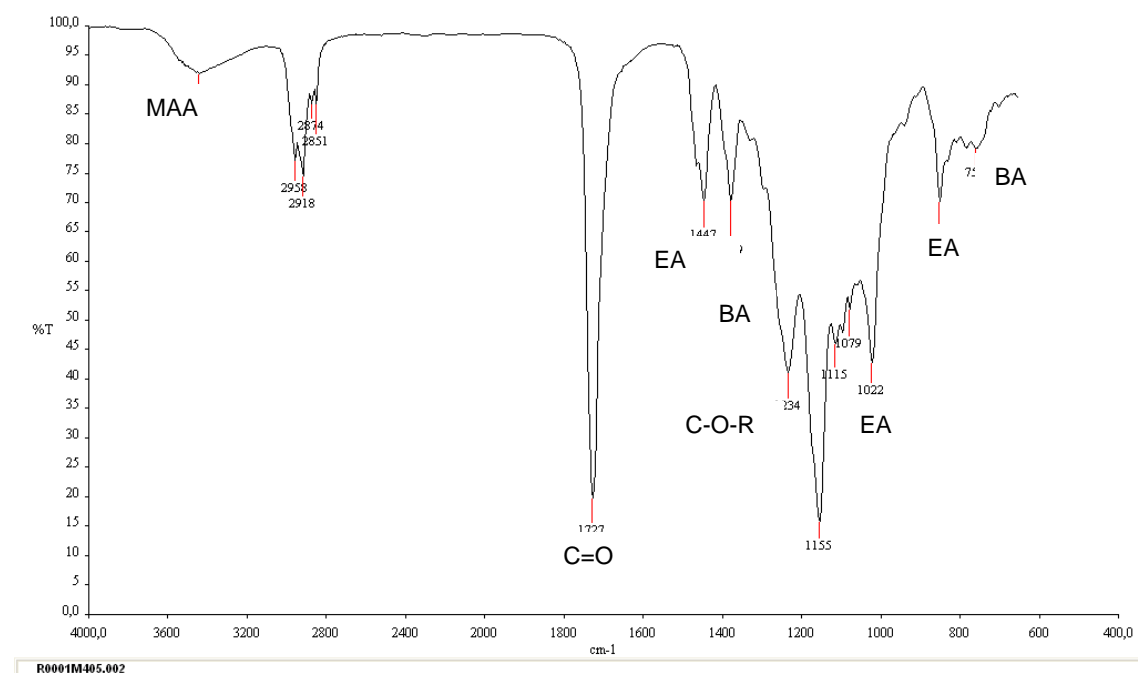


Figure 2. Infrared spectrum of the synthesized resin

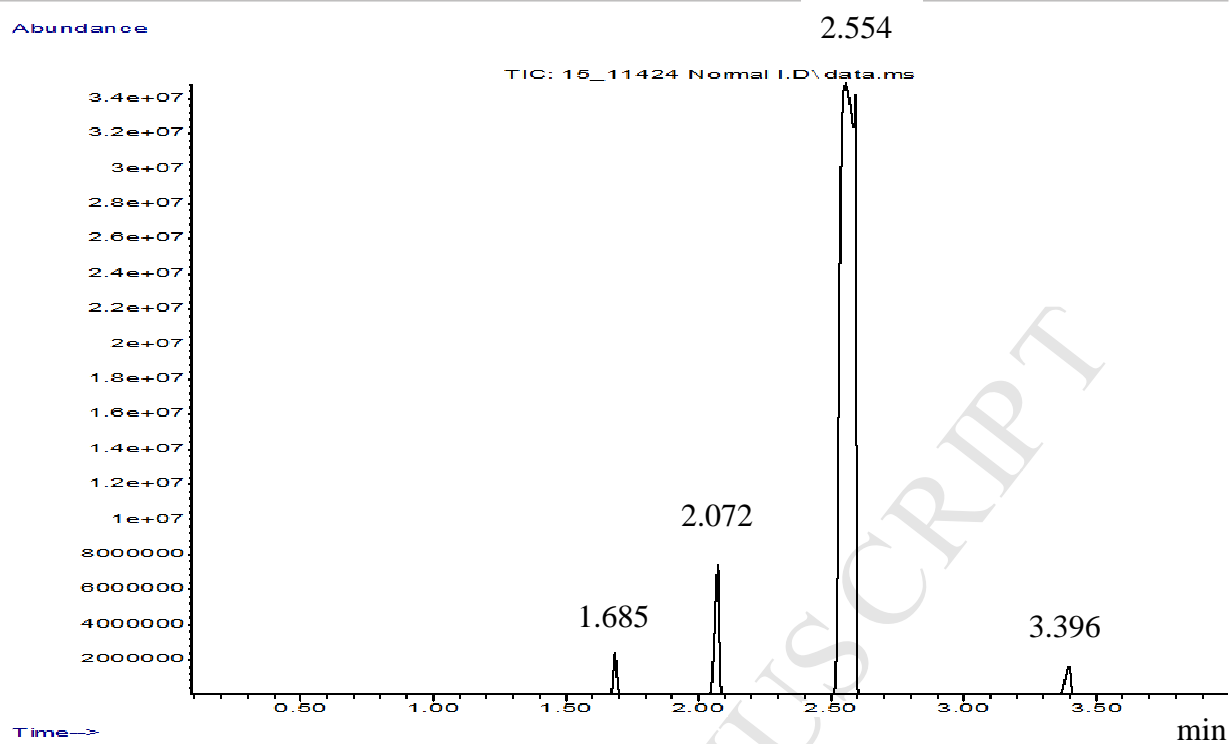


Figure 3. Chromatogram of the measurement using the commercial acrylic resin

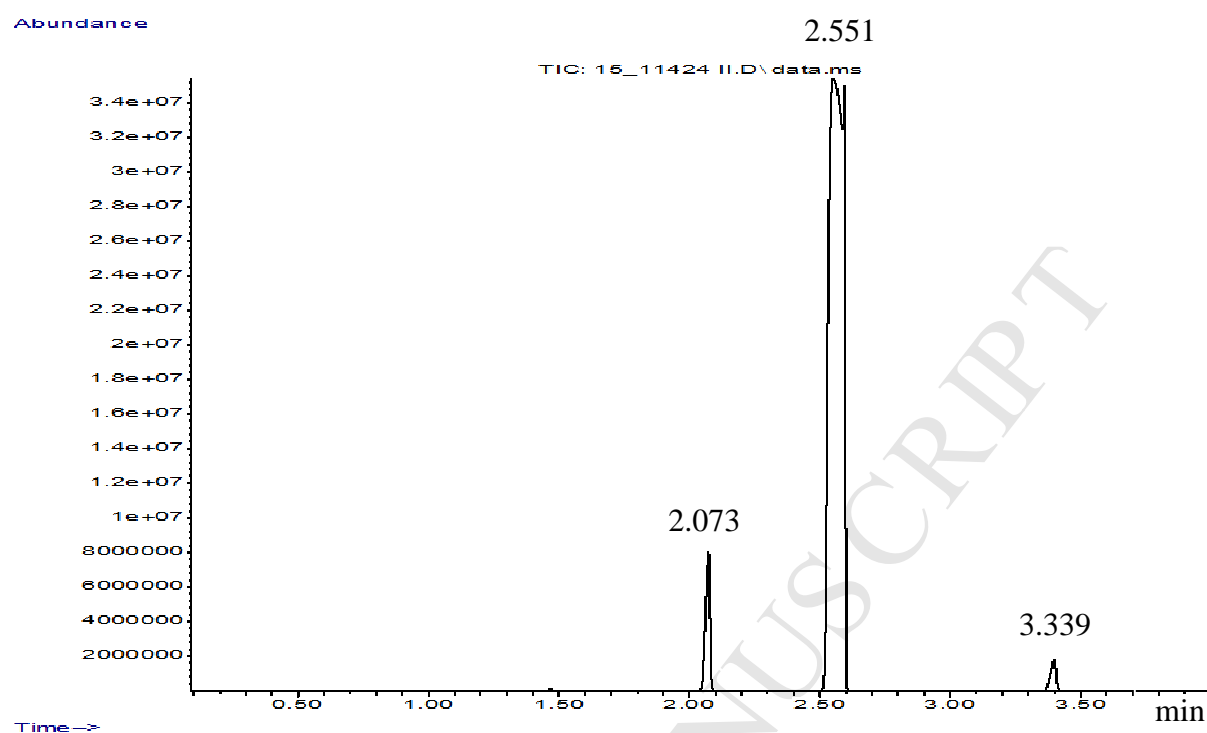


Figure 4. Chromatogram of the measurement using the new synthesized resin

Development of a new leather impregnation finishing.

The process is free of VOCs.

The system is not classified as hazardous.

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